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Chain dynamics in mesoscopically confined polymer melts. A field-cycling NMR relaxometry study

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Abstract

Polymer chain dynamics were studied with the aid offield-cycling NMR relaxometry (time scale: 10-9s⋯10-4s) supplemented by field gradient NMR diffusometry(time scale: 10-4s⋯100s). Three sorts of samples of mesoscopically confined polymer melts were examined. In the first sample series, linear poly(ethylene oxide) was incorporated in strands embedded in a quasi-solid and impenetrable methacrylate matrix. The strand diameters ranged from 10 to 60 nm. It was shown that chain dynamics becomes dramatically different from bulk behavior. This so-called "corset effect" occurs both above and below the critical molecular mass and reveals dynamic feature spredicted for reptation. On the time scale of spin-lattice relaxation, the frequency and molecular weight, signature of reptation, T1 ~ M0v3/4, that is limit II ofthe Doi/Edwards formalism corresponding to the mean squared segment displacement law (r2) ~ M0 t1/4, showed up. A "tube" diameter of only 0.6 nm was concluded to be effective on this time scale even when the strand diameter was larger than the radius of gyration of the PEO random coils. The corset effect is traced back to the lack of the local fluctuation capacity of the free volume under nanoscopic confinements. The confinement dimension at which the cross-over from confined to bulk chain dynamics is expected was estimated to be micrometers. Using the so-called roll-coating technique, micrometer thick polymer melt layers between Kapton foils were prepared. Perceptible differences from the bulk materials were found. The polymer species studied in this case was perfluoropolyether with Flory radii in the order of 7 nm. Remarkably, the confinement effect was shown to reach polymer-wall distances of the order 100 Flory radii. As a third confinement system, melts of perfluoropolyether were filled into a porous silica glass (Vycor; 4 nm nominal pore size). In this case, a crossover from Rouse dynamics in the bulk to reptation in the Doi/Edwards limit III (T1 ~ M-1/2v1/2 corresponding to (r2) ~ M-1/2t1/2) was observed.

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